B. AVERAGE GAS HOLD-UP MEASUREMENTS

For a two-phase system, the average gas hold-up is defined as the volume percent of gas in the dispersion. A knowledge of the gas hold-up is necessary for reactor design, since it allows the estimation of the residence time of the gas in the reactor. The gas hold-up, together with the Sauter mean diameter, also determines the specific interfacial area available in the dispersion for mass transfer. Experiments were conducted with the FT-300 - nitrogen system in the two bubble columns (0.051 and 0.229 m ID) to measure the average gas hold-up. The effects of the various operating and design parameters on the gas hold-up were investigated. A limited number of experiments were also conducted with FT-200 wax, Sasol's Arge reactor wax, Mobil reactor wax and distilled water, to study the effect of liquid medium on the average gas hold-up.

B.1. Operating Procedure

The average gas hold-up was measured by visual observations of the expanded height of the dispersion (H) and the static liquid height (H_s), and its value was calculated from

$$\epsilon_g = \frac{H-H_s}{H} \times 100 \qquad (V-1)$$

The first reading of the expanded height was made 20-30 minutes after the desired column temperature and gas flow rate were reached. These readings were repeated a minimum of three times for a given set of operating conditions, with a 20-30 minute time interval between two successive measurements to ensure that the steady state was achieved. In general, for velocities < 0.05 m/s, the readings were 30 minutes apart; whereas, for velocities greater than 0.05 m/s, the readings were 20 minutes apart. For some experiments, the expanded height did not stabilize during the three measurements. In these cases, additional measurements were made until the expanded height stabilized. This was particularly necessary when foam was present at the top of the dispersion. After the last measurement for a given set of conditions the valve below the column was closed and the main flow of nitrogen stopped. The static liquid height was measured after all of the gas disengaged from the dispersion.

The static liquid height was maintained at approximately 2.0 m for majority of the experiments. For experiments conducted in the 0.051 m ID column with the 40 μm SMP distributor, static heights as low as 0.6 m were used in order to contain the foam within the column.

Several runs were made with the same batch of wax. A new batch of wax was used once the old wax began to turn yellow. APPENDIX A outlines the guidelines used for wax changes and the procedure used to clean the apparatus between runs or between wax changes. The numbering scheme employed to distinguish the different runs (see APPENDIX A) reflects the wax batch number and the run number with a given batch of wax. A summary of the different runs and operating conditions is also included in APPENDIX A.

B.2. Reproducibility and Effect of Operating Procedure

The reproducibility of average gas hold-up measurements with the FT-300 - nitrogen system is significantly affected by the operating procedure employed, and to some extent by the age of the wax or the time on stream for a given batch of wax. Experiments were conducted in the 0.051 m ID and 0.229 m ID glass columns to investigate the magnitude of these effects. The 1.85 mm and 4 mm orifice plate, and a 40 μm sintered metal plate (SMP) distributors were used in the 0.051 m ID column, whereas the 19 X 1.85 mm perforated plate distributor was used in the 0.229 m ID column. The discussion below is based on results from 4 runs with the SMP distributor, 4 runs with the 4 mm distributor, and 12 runs with the 1.85 mm distributor conducted in the 0.051 m ID column at 265°C. In addition, 4 runs were conducted using the 19 X 1.85 mm distributor at 265°C in the 0.229 m ID column. Limited number of runs were made at 160, 200, 230 and 280°C using the various distributors in the two columns. The gas velocity in majority of the runs was in the range 0.01 to 0.12 m/s.

The major highlights of these investigations are:

- For temperatures in the range 230-280°C, there is a range of gas velocities over which two values of gas hold-up are possible with FT-300 wax for all columns and distributor types investigated. In a system with molten paraffin wax as the liquid medium this type of behavior has been observed for the first time. The higher gas hold-ups are accompanied by the presence of foam, therefore, this mode of operation is referred to as the "foamy" regime. In the absence of foam, "slug flow" prevails in the 0.051 m ID column, whereas flow in the 0.229 m ID column is in the "churn-turbulent" regime. At low gas velocities ($u_g < 0.02$ m/s), when foam is not present, the "homogeneous bubbling" regime prevails.
- The start-up procedure determines which flow regime will be attained, with increasing order of gas velocities favoring the "foamy" regime. A transition from the "foamy" to the "slug flow" or "churn-turbulent" regime occurs when u_g exceeds a certain critical value, and the transition to the "foamy" regime occurs when u_g drops below a certain critical value. Since the two critical velocities are different, a

hysteresis loop is created.

- When multiple runs, under similar conditions, are conducted with a given batch of wax, hold-up in the "foamy" regime increases with age of the wax, which might be caused by the breakdown of FT-300 wax when subjected to high temperatures for a significant length of time. Thus, foaming occurs over an extended range of velocities for older wax compared to fresh wax and there is a corresponding change in the velocity at which the transition from the "foamy" regime to the "slug-flow" or "churn-turbulent" regime occurs.
- Long term stability studies reveal large variations in hold-up with time in the "foamy" regime, and relatively low variations in the absence of foam. This causes problems with reproducibility of hold-up measurements in the presence of foam.
- Reactor waxes do not show hysteresis behavior and there is no significant effect of operating procedure.

B.2a. Effect of Start-up Procedure

Figure V-10 illustrates a typical example of hysteresis behavior with FT-300 wax at 265°C in the 0.051 m ID column using the 1.85 mm orifice plate distributor. When increasing order of gas velocities were employed (open symbols), the gas hold-up increased rapidly in the velocity range 0.01-0.03 m/s largely due to the presence of a foam layer at the top of the gas-liquid dispersion. The foam breakup, accompanied by a substantial decrease in the gas hold-up, occurred when the velocity was increased from 0.03 m/s to 0.04 m/s. This breakup may be attributed to the presence of rising slugs. Upon further increasing the gas velocity, foam was not

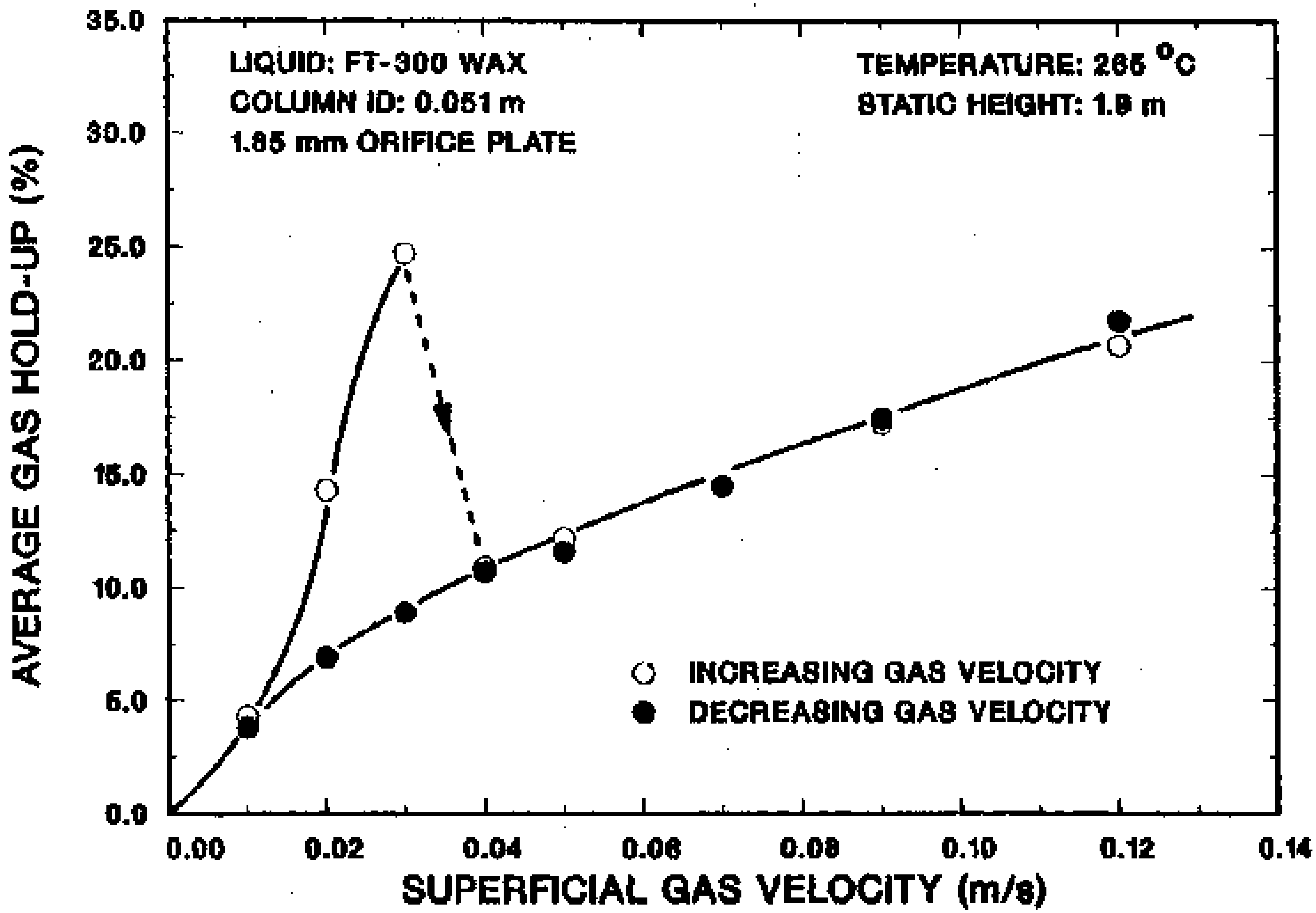

Figure V-10. Effect of start-up procedure and superficial gas velocity on gas hold-up (open symbols - Run 4-1 indicate a start-up velocity of 0.01 m/s; solid symbols - Run 4-2 - indicate a start-up velocity of 0.12 m/s) observed and the gas hold-up increased gradually. In a run conducted using decreasing order of velocities (solid symbols), nearly the same hold-ups (as in the run with increasing order of velocities) were obtained for velocities in the range 0.04-0.12 m/s. However, during this run foaming did not take place even at low gas velocities (0.01-0.03 m/s). In a system with molten paraffin wax as the liquid medium this type of behavior has been observed for the first time.

The mode of operation where foam is present will be referred to as the "foamy" regime. In this regime a stable layer of foam exists on the top of the liquid level, giving rise to higher hold-ups. Visual observations of the flow field show the presence of slugs or slug type bubbles at velocities greater than about 0.03 m/s. Under these conditions, if no foam is present, the mode of operation will be referred to as the "slug flow" regime. At lower gas velocities (u_g < 0.02 m/s), when foam is not present, visual observations indicate an almost uniform bubble size distribution, indicating that the flow might be in the transition or the "homogeneous bubbling" regime.

In general, all runs conducted in the temperature range 230-280°C exhibited hysteresis with respect to the hold-up values. However, the variation of gas hold-up with velocity, for runs conducted using decreasing order of velocities, was not always the same as that shown in Figure V-10. There were instances when foam also appeared in these runs and a transition from the "slug flow" to the "foamy" regime occurred. Nevertheless, the velocity at which this transition occurred was always lower than the velocity at which the transition from the "foamy" to the "slug flow" regime occurred when increasing order of velocities were employed. Figure V-11

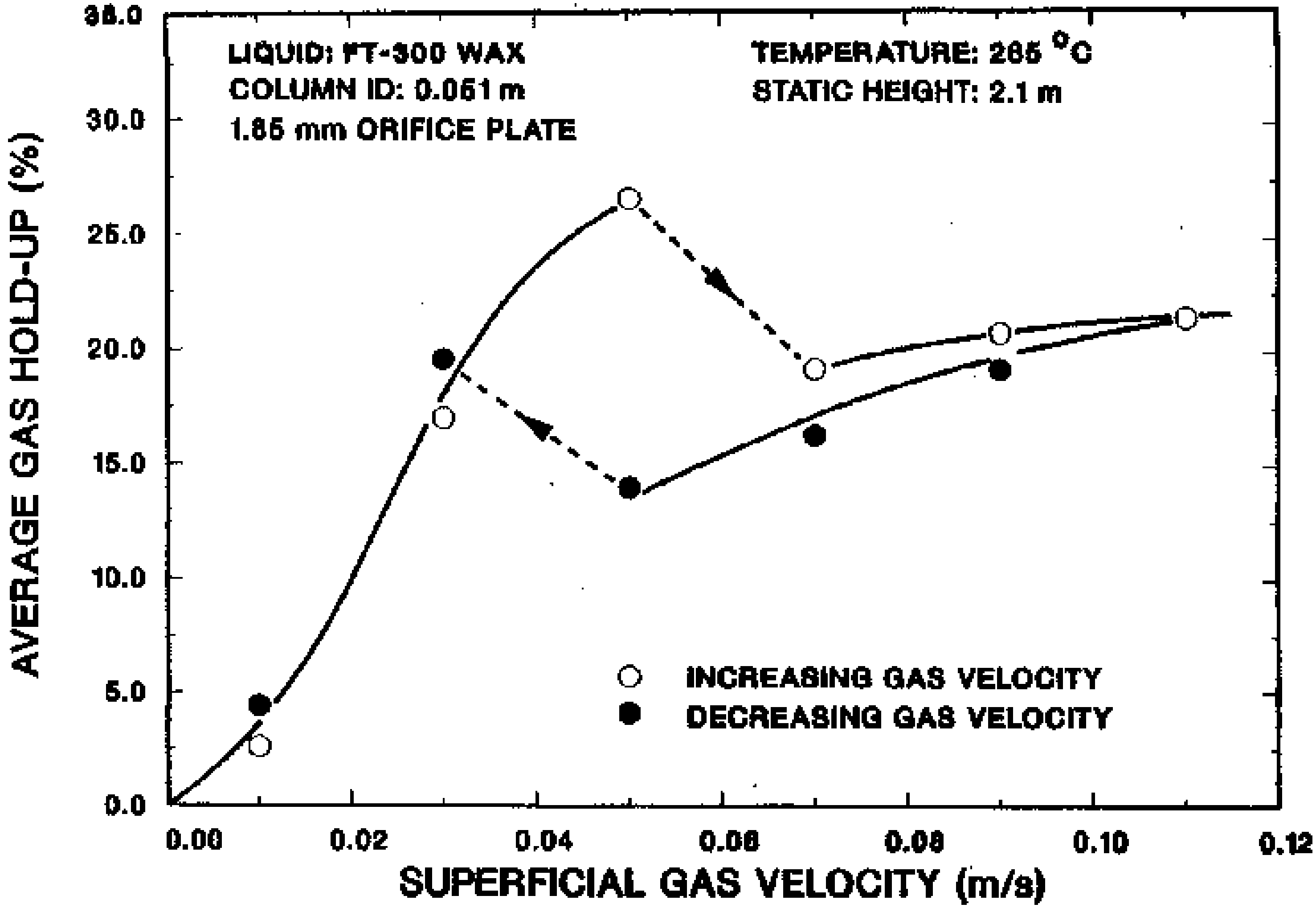

Figure V-11. Effect of operating procedure and superficial gas velocity on gas hold-up (Run 3-2) shows an example of a run in which foam reappeared when gas velocity was changed from 0.05 m/s to 0.03 m/s, when decreasing order of velocities were used. Measurements made using the 4 mm orifice plate distributor in the 0.051 m ID column, under similar conditions, showed behavior which is qualitatively similar to that for the 1.85 mm orifice plate distributor in the temperature range 230-280°C.

Figure V-12 shows the effect of operating procedure on average gas hold-up for runs conducted using the 40 μm sintered metal plate (SMP) distributor at 265°C. When the run was conducted using increasing order of velocities (open symbols), the average gas hold-up increased rapidly in the velocity range 0.01-0.02 m/s as foam filled the entire column. The gas hold-up remained fairly constant in the velocity range 0.02-0.09 m/s; however, upon further increasing the gas velocity to 0.12 m/s the hold-up decreased significantly. This transition from the "foamy" regime to the "slug flow" regime is not complete and it is possible that a lower hold-up would be obtained at 0.12 m/s by extending the duration of run at this velocity. For the run conducted using decreasing order of velocities (solid symbols), with a start-up velocity of 0.12 m/s, foam did not appear until the gas velocity was decreased to 0.04 m/s, when a sudden increase in hold-up was observed. The hold-up values in the velocity range 0.04 m/s to 0.01 m/s are very similar to those obtained using increasing order of velocities. These results are qualitatively similar to those observed with the 1.85 mm distributor.

Figure V-13 shows results from a run conducted in the 0.229 m ID column with FT-300 wax at 265°C using a 19 X 1.85 mm perforated plate distributor. In this run increasing order of velocities were followed by

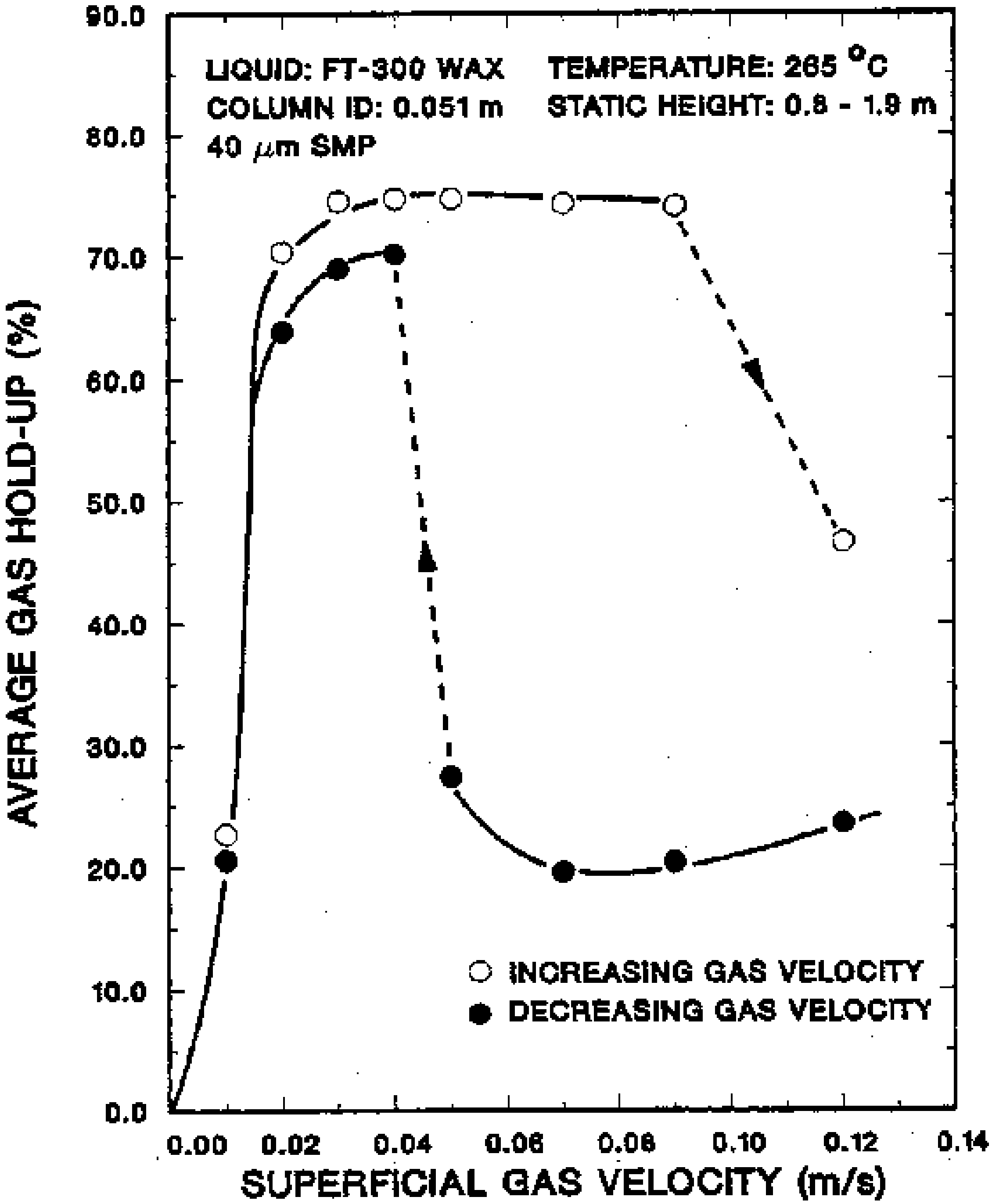

Figure V-12. Effect of start-up procedure and superficial gas velocity on gas hold-up (open symbols - Run 5-1 - indicate a start-up velocity of 0.01 m/s, solid symbols - Run 5-2 - indicate a start-up velocity of 0.12 m/s)

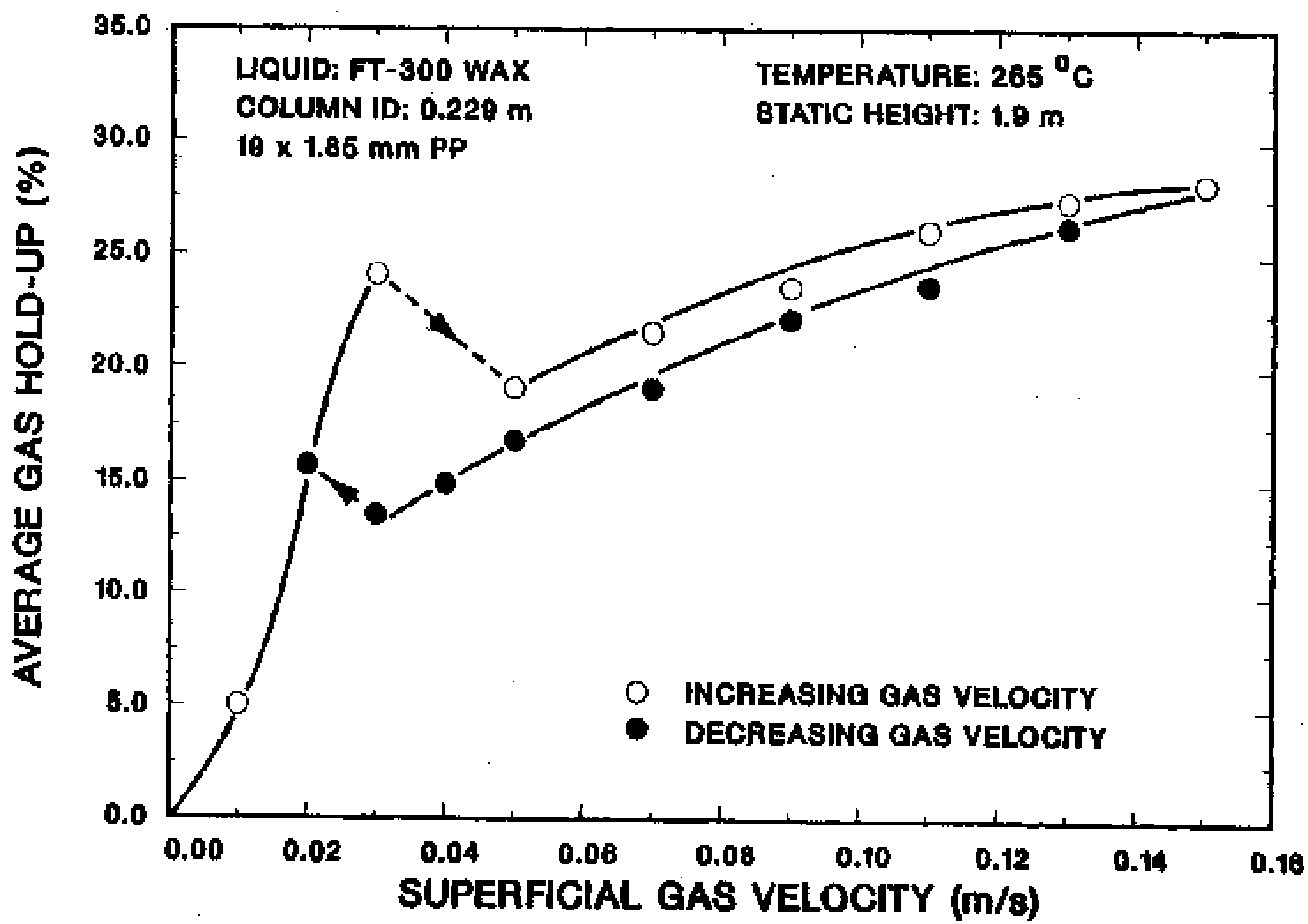

Figure V-13. Effect of operating procedure and superficial gas velocity on gas hold-up (Run 1-3) decreasing order of velocities in the same run. These results once again illustrate the existence of two values of gas hold-up in the velocity range 0.02-0.05 m/s, with higher hold-up produced using increasing order of velocities (open symbols). The hold-up values in the absence of foam are somewhat higher for increasing order of velocities compared to decreasing order of velocities in the velocity range 0.05-0.13 m/s. These differences can be explained in terms of better mixing of the various surface active impurities into the dispersion with time elapsed, therefore, hold-up values later on in the run (when mixing is better) are lower than earlier in the run. Visual observations of the dispersion, in the absence of foam, showed intense mixing and the flow appears to be in the "churn-turbulent" flow regime. This is unlike the 0.051 m ID column, where "slug flow" exists in the absence of foam. In general, hysteresis effects were not as pronounced and reproducibility was much better in the 0.229 m ID column as compared to the 0.051 m ID column.

Studies were also conducted with reactor waxes in order to investigate the effect of operating procedure on the average gas hold-up. Results from these studies (see Section V-B.7.) show that reproducibility of hold-up values is significantly better with reactor waxes than with FT-300. Also, the operating procedure does not appear to have an effect on the average gas hold-up values and the hysteresis type of behavior was not observed.

The only known case of foam breakup in literature with a wax as the liquid medium was reported by Farley and Ray (1964a). Their studies, using the Krupp wax as the liquid medium in a 0.235 m ID reactor, showed that a transition from the "foamy" to the "churn-turbulent" regime took place within an hour of increasing the superficial gas velocity from 0.03 m/s to

0.06 m/s.

A theoretical basis for the existence of two values of the gas hold-up for a given set of operating conditions was established earlier (e.g. Wallis, p.92, 1969; Riquarts, 1979), however, experimental evidence demonstrating this type of behavior is rather scarce. In studies by Anderson and Quinn (1970) and Maruyama et al. (1981) with the air/tap water system the hysteresis type of behavior was observed. The "foamy" regime, in both studies, was obtained in experiments conducted using increasing order of velocities. A possible explanation for the breakup of foam and for the effect of start-up procedure on foaming was given by Anderson and Quinn and could be extended to explain the similar behavior of FT-300 wax. They postulated that at low gas velocities surface-active impurities, which act as coalescence promoters, diffuse gradually and accumulate at the top of the dispersion. However, once their concentration exceeds a critical level rapid coalescence takes place resulting in the formation of slugs. Once the slugs are formed at the top of the column, the impurities are dispersed back into the bulk of the liquid through intensive mixing and turbulence which accompanies slug formation. This in turn causes the slugs (large bubbles) to form at lower heights in the dispersion, thus preventing foaming. Similarly, when a run is started at a high velocity (decreasing order of velocities), the impurities are thoroughly dispersed throughout the column hampering the formation of foam even when velocities are sufficiently low. However, in some instances (e.g. the run using decreasing order of velocities in Figure V-11) the concentration gradients become steeper as the impurities begin to accumulate at the top, leading to the development of foam after some time. This theory could also be used to offer a possible explanation for the higher hold-ups obtained in the "churn-turbulent" regime when increasing order of velocities were used compared to those obtained for decreasing order of velocities in the 0.229 m ID column (Figure V-13). Once the foam broke in this run, the impurities began to mix into the bulk of the dispersion, however, this is not an instantaneous process, and it is possible that a steady state was not reached when the increasing order of velocities were being used. Therefore hold-up values were slightly higher with increasing order of velocities (earlier in the run - shorter mixing time) compared to values with decreasing order of velocities (later in the run - longer mixing time). The better reproducibility in the 0.229 m ID column compared to the 0.051 m ID column could be attributed to the better mixing of surface active agents in the larger column.

B.2b. Effect of Wax Aging

Figures V-14 and V-15 illustrate the effect of the aging of wax on the average gas hold-up in the 0.051 m ID and the 0.229 m ID columns, respectively. In both cases, the effect of aging primarily affects hold-up values in the "foamy" regime. For the 0.051 m ID column results from three runs conducted using the same batch of wax are presented in Figure V-14. For relatively fresh wax the hold up values (indicated by circles in Figure V-14) show no foaming for the range of superficial gas velocities employed (0.02-0.15 m/s), however, for a later run with the same batch of wax (indicated by triangles) foam appeared in the velocity range 0.02-0.03 m/s and broke as velocity was increased to 0.04 m/s. This particular run was stopped once the foam broke. A run conducted after further aging of the wax (indicated by squares) resulted in foam being produced over a relatively

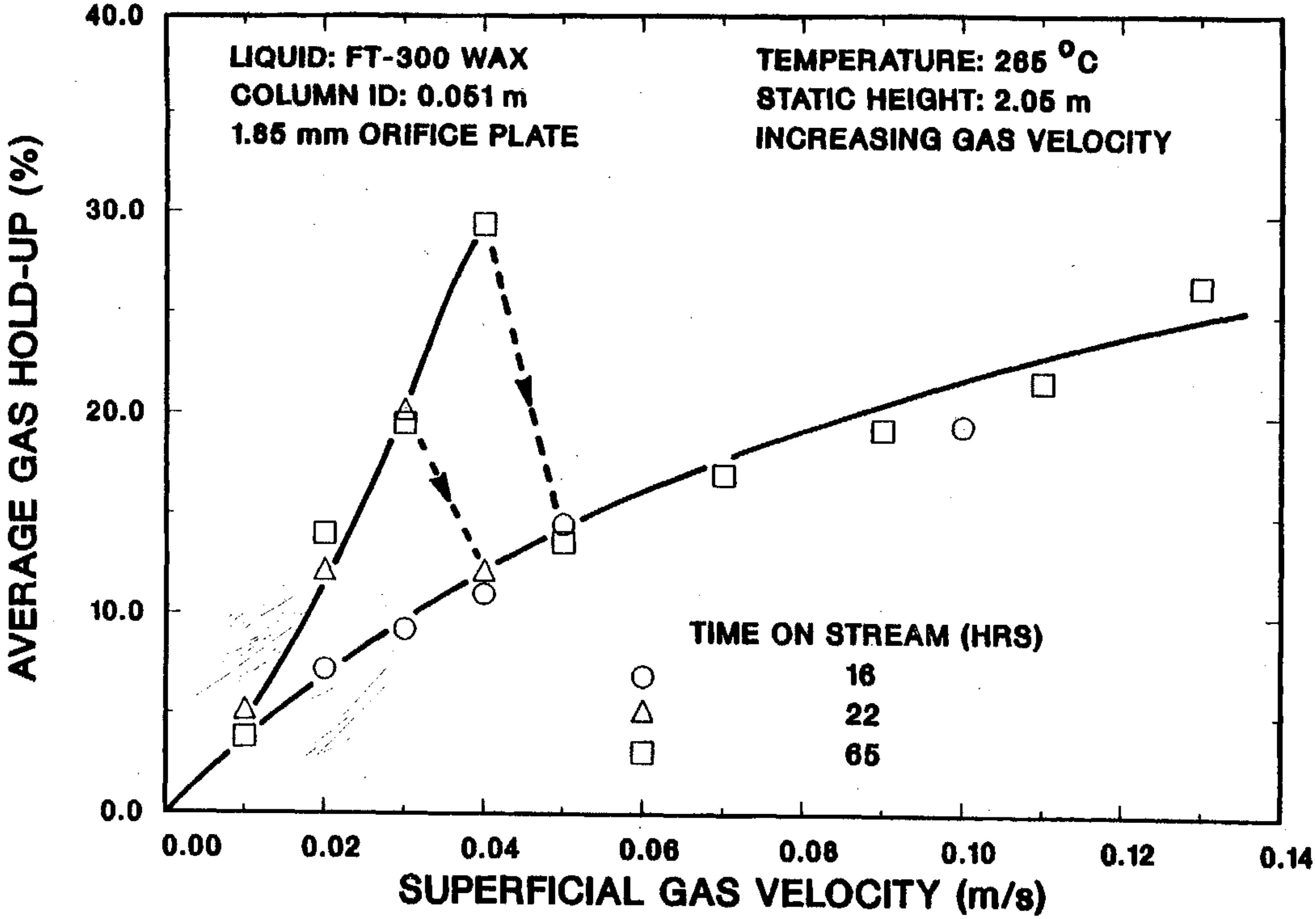

Figure V-14. Effect of wax aging on gas hold-up (○ - Run 2-3; △ -Run 2-4; □ -Run 2-7)

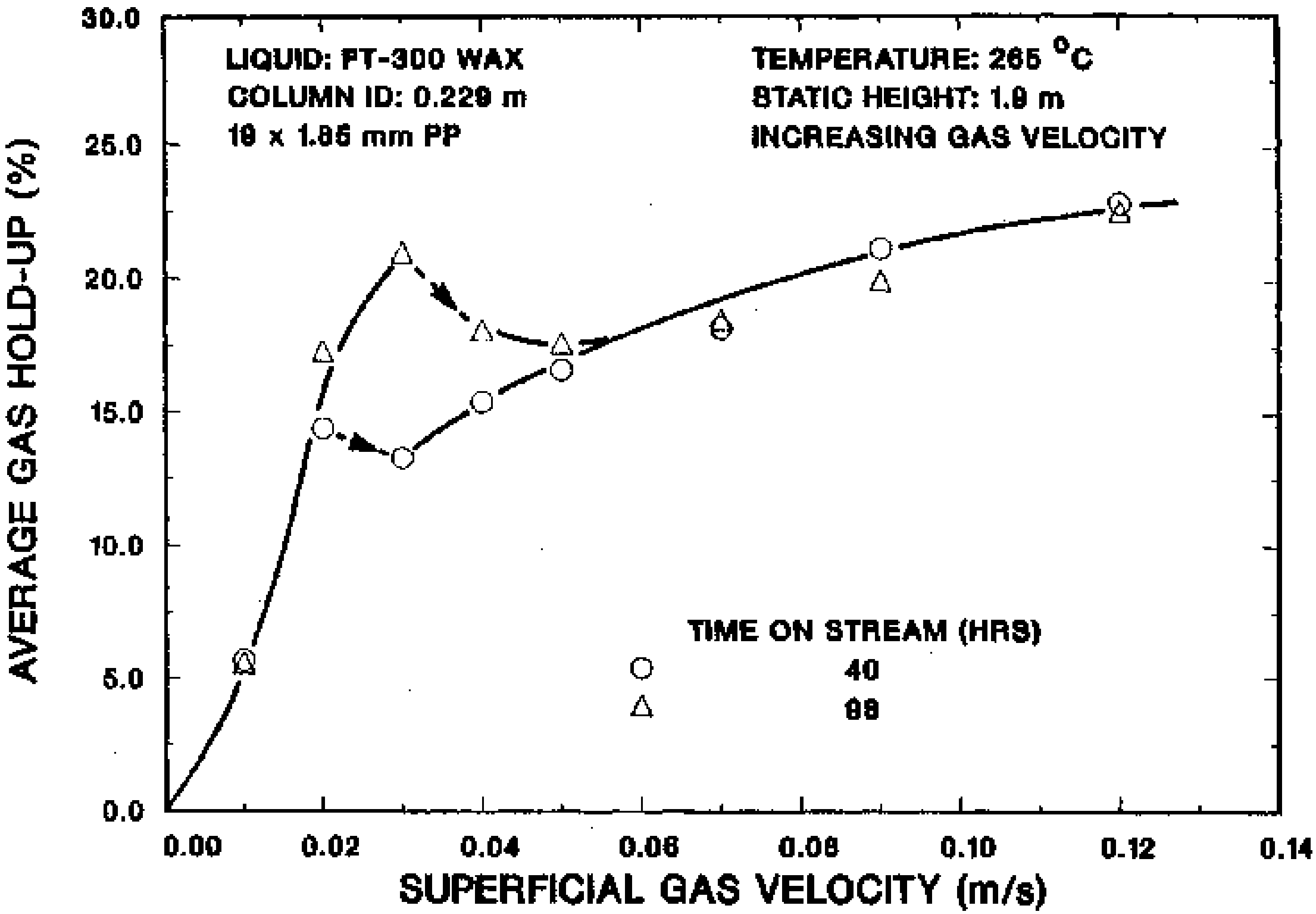

Figure V-15. Effect of wax aging on gas hold-up (○- Run 2-3; △-Run 2-8) larger velocity range (0.02-0.04 m/s) and a corresponding delay in the breakage of foam (at 0.05 m/s compared to 0.04 m/s) was observed. The hold-up values in the absence of foam (u_g greater than 0.04 m/s) are essentially similar for the different runs. Results from two runs in the 0.229 m ID column (Figure V-15) are qualitatively similar to those from the 0.051 m ID column. The older wax once again showed foaming over a prolonged range of gas velocities, thus delaying the breakage of foam until 0.03-0.04 m/s compared to 0.02 m/s for the fresher wax. Hold-up values in the absence of foam are once again similar for the two runs. The effect of wax aging was similar for all runs irrespective of column diameter and distributor type.

B.2c. <u>History Effects</u>

Results from the run made in the 0.229 m ID column, presented in Figure V-13, show history effects. The consistently lower hold-up values, in the absence of foam, for decreasing order of velocities were a direct consequence of the history of the run as discussed previously. Figure V-16 compares results from two runs conducted with different operating procedures. The two runs were made one after the other with the same batch of wax, thus minimizing the effect of wax aging. When a start-up velocity of 0.01 m/s was used, hold-up values were as expected, showing a "foamy" regime followed by a transition to the "slug flow" regime (open circles). However, when an odd order of velocities was used (solid circles), with a start-up velocity of 0.09 m/s, hold-up increases as velocity is increased to 0.17 m/s (no foam was present). The gas hold-up values are consistently higher than in the previous run. Upon decreasing the velocity the same curve is followed up to 0.09 m/s, but at lower gas velocities the hold-up starts increasing and passes through a maximum at about 0.06 m/s (ϵ_g -

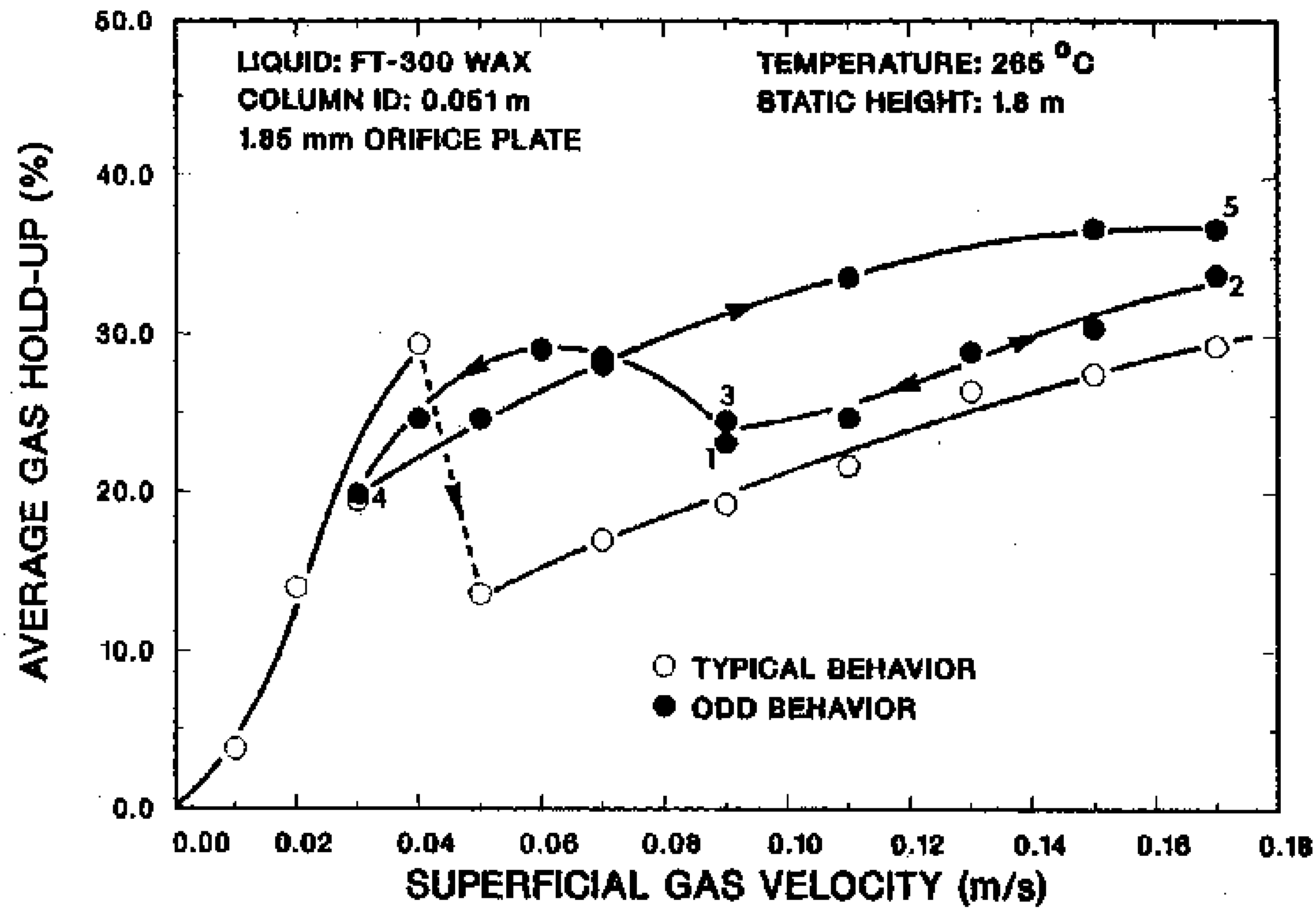

Figure V-16. Effect of run history and superficial gas velocity on gas hold-up (open symbols - Run 2-7; solid symbols - Run 2-8 - numbers on the curve indicate order of velocities employed)

29%), and then decreases, coinciding with the value from the purely increasing velocity curve at 0.03 m/s. When velocity was further increased from 0.03 to 0.17 m/s, the transition from the "foamy" to the "slug flow" regime did not take place. It appears that the history of the run, with respect to gas velocities, has an effect on hold-up values. This is not typical of the results obtained from the various runs and the reasons for this kind of behavior are not clear. This experiment illustrates the difficulties in obtaining reproducible results with a system that has a tendency to produce foam.

B.2d. Long Term Stability Studies

The long term stability runs were conducted with a run time of 4 hours per velocity using the 1.85 mm orifice plate distributor at 265°C in the 0.051 m ID column. The wax was drained to the storage tank after each velocity, therefore, it is expected that these results are independent of the operating procedure. Hold-up was measured every 15 minutes during the first hour and every 30 minutes during the subsequent 3 hours. Results from this study are presented in Figure V-17 (indicated by open circles). The vertical bars at each velocity indicate the range in which the hold-up values varied at that particular velocity. The open circles indicate an average of the eight hold-up values for each velocity. These results illustrate the large variability in hold-up values in the "foamy" regime, indicating problems with reproducibility of results in this regime. The variability in the "slug flow" regime is much smaller. These results also lend further support to the theory postulated by Anderson and Quinn. At low velocities, which are not conducive to mixing (0.01-0.04 m/s), the build-up of steep gradients of the surface active impurities occurs over a period of

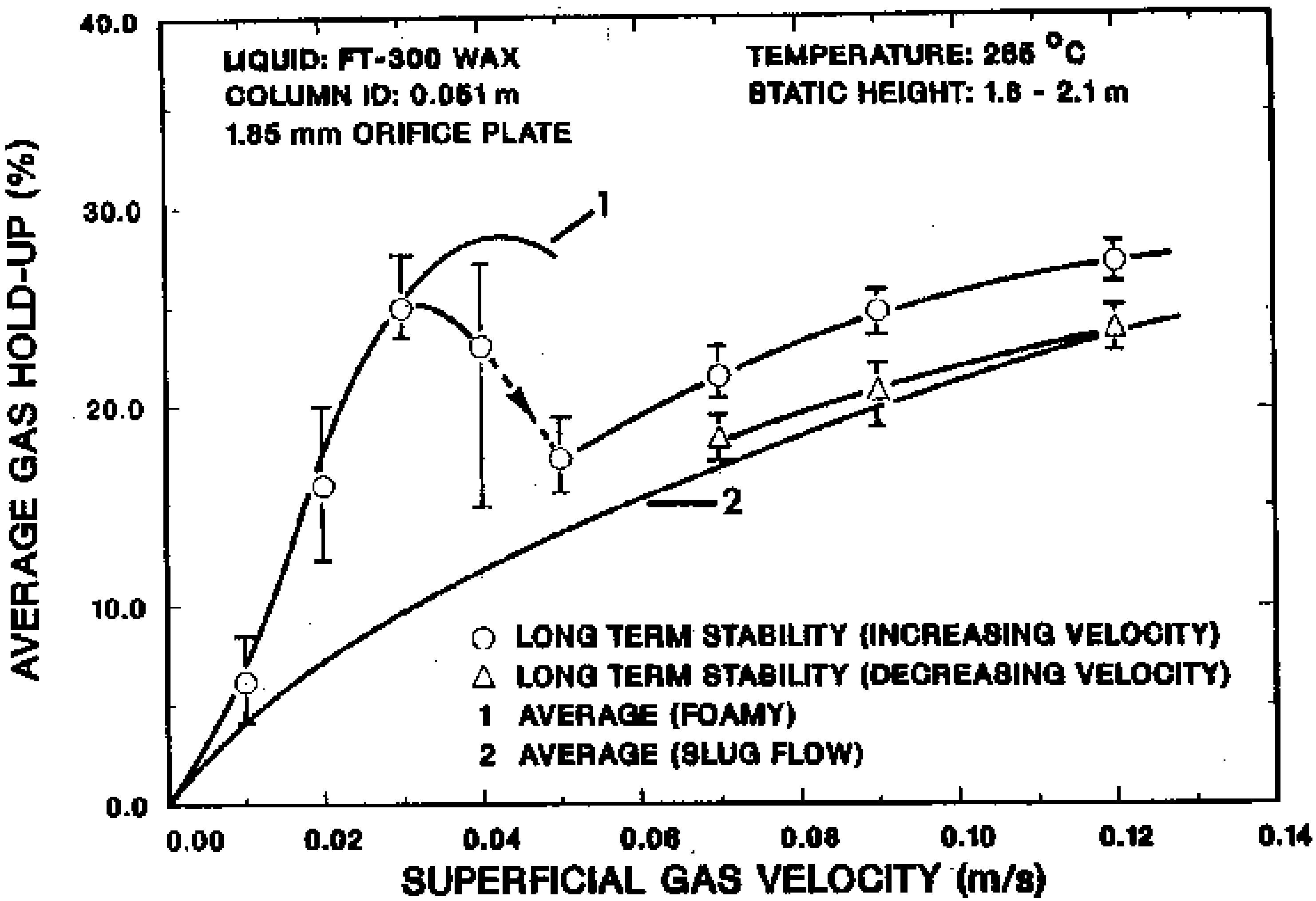

Figure V-17. Results from long term stability studies with FT-300 wax and comparison with average values from other runs (symbols - arithmetic mean of hold-ups at a given velocity; vertical bars - range in which hold-ups varied at that velocity; ○ - Run 6-1 - indicate a start-up velocity of 0.01 m/s; △ - Run 7-3 - indicate a start-up velocity of 0.12 m/s; curves 1 & 2 - arithmetic averages from 12 runs) time and therefore, foaming is observed at these velocities. However, for velocities greater than 0.04 m/s, mixing is much improved and the impurities are uniformly distributed in the bulk of the liquid, preventing foaming and resulting in lower hold-up values. Therefore, even though these results are independent of start-up velocity, the behavior is similar to that observed with increasing order of velocities.

In the run discussed above, the age of wax increased with velocity, since the first set of data were obtained at 0.01 m/s (fresh wax), and velocity was progressively increased up to 0.12 m/s (oldest wax). Additional runs were therefore conducted to isolate the effect due to the aging of wax. Results from these runs are indicated by triangles in Figure V-17. The duration per velocity and the frequency of hold-up measurements were the same as in the previous run. However, for this case wax was relatively fresh at 0.12 m/s and it aged as gas velocity was progressively lowered. As expected, hold-up values for this run were substantially lower in the range of velocities investigated (0.07-0.12 m/s), lending further support to the effect of wax aging.

Figure V-17 also shows average values for gas hold-up measurements from several runs conducted at 265°C in the 0.051 m ID column using increasing/decreasing order of velocities. These values were obtained using hold-up values from a total of eight runs conducted using increasing order of velocities and a total of four runs conducted using decreasing order of velocities. The average values (curves 1 and 2) for both the "foamy" and "slug flow" regimes are presented. These results show that the "foamy" regime could be maintained only up to 0.05 m/s. Results from long-term stability runs, after accounting for wax aging, are in good agreement with the average value curves.

The above investigations indicate that the reproducibility of hold-up values in a system which has a capacity to foam, is dependent on a complex interaction between a number of factors. Some of these factors, such as the operating procedure, can be controlled independently. Whereas, effects due to the aging of wax, and the amount of foam produced, are not as predictable. Our study shows that it is possible to eliminate foaming by using a relatively high start-up velocity.

B.3. Effect of Temperature

The effect of temperature on gas hold-up was investigated for temperatures between 160 and 280°C. Experiments were done in the 0.051 m ID and the 0.229 m ID glass columns using FT-300 wax. The 40 μm SMP and 1.85 mm orifice plate distributors were used in the 0.051 m ID column, whereas the 5 X 1 mm, 19 X 1 mm and the 19 X 1.85 mm perforated plate distributors were employed in the 0.229 m ID column. Results from these experiments can be summarized as follows:

- In the "foamy" regime, an increase in temperature is accompanied with an increase in foam, and thus higher hold-up values.
- In the absence of foam, hold-ups showed a marginal decrease with a decrease in temperature.
- It was possible to avoid foaming by operating at sufficiently low temperatures (e.g. 160°C with the 1.85 mm orifice plate distributor in the 0.051 m ID column or at 170°C with the 5 X 1 mm perforated plate distributor in the 0.229 m ID column).

Results from runs with FT-300 wax in the 0.051 m ID column using the 1.85 mm orifice plate distributor at four different operating temperatures